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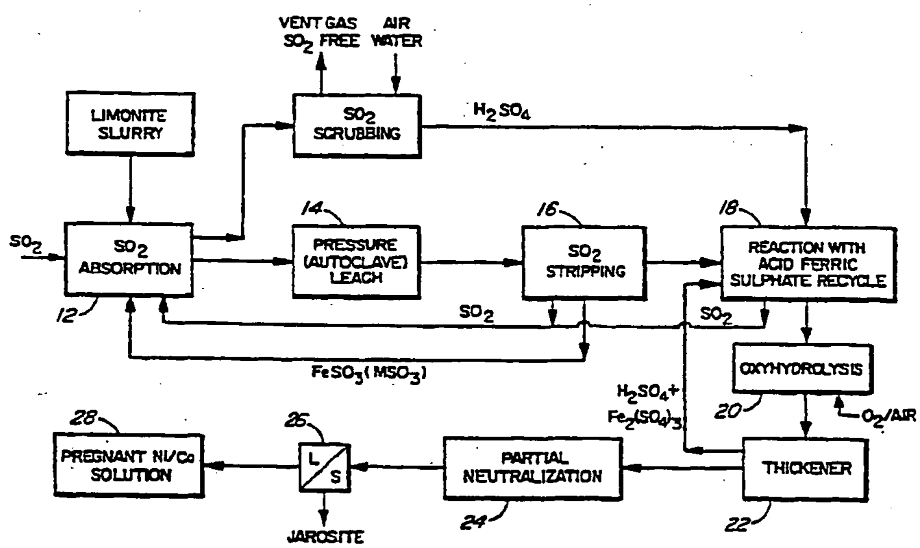
(54) Title: PROCESS FOR EXTRACTION OF NICKEL AND COBALT FROM LATERITE ORES



(57) Abstract

A process for the extraction of nickel and cobalt from a laterite ore comprises the step of reacting the ore, in slurry form, with sulphur dioxide to convert the iron, nickel and cobalt in the ore to soluble sulphates and bisulphites in a product slurry. In a specific embodiment of the process, the product slurry is further treated to convert the bisulphites to sulphates and to precipitate iron as jarosite. An essentially iron free solution of nickel and cobalt is produced from which nickel and cobalt can be recovered by one or a combination of known methods.

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PROCESS FOR EXTRACTION OF NICKEL AND COBALT FROM LATERITE ORES

FIELD OF THE INVENTION

This invention relates to a process for extracting nickel and cobalt from laterite ores.

BACKGROUND OF THE INVENTION

A high proportion of known world resources of nickel and cobalt are contained in laterite deposits. These deposits are typically derived from weathering of mainly magnesium silicate minerals, such as garnierite, which contain nickel and cobalt, as well as iron, aluminum, chromium and a wide range of trace elements.

Geologically, a profile of a fully developed laterite deposit comprises a high iron surface layer (ferricrete) with low nickel and cobalt content; a layer of limonite containing mainly iron oxides, typically more than 40% Fe dry basis, plus nickel-cobalt values; a layer of saprolite, which contains partially weathered magnesium silicate minerals, enriched in nickel and cobalt; fractured but largely weathered garnierite; and basement unweathered garnierite.

The present invention relates mainly to the limonite portion of lateritic nickel-cobalt deposits. However, the saprolite and weathered garnierite zones of suitable deposits may be used to advantage within the process.

There are process energy cost advantages inherent to processes which treat laterites by direct leaching, as opposed to roasting, which is a dry process

taking place at high temperature, and which requires substantial energy input to evaporate the free and hydration water associated with typical laterite ores.

The principal commercial method involving direct hydrometallurgical treatment of limonitic nickel-cobalt ores is that practised at the Moa Bay mine in Cuba. This process involves high temperature, i.e., greater than 400°F (200°C), sulphuric acid leaching of laterite. To operate the leach at a temperature greater than 400°F, high pressure reaction vessels are required to maintain the sulphuric acid-water leach solution in the liquid phase.

The main advantage of the present invention compared to previously disclosed methods arises from essentially complete dissolution of metal oxide components of limonite, i.e., iron, nickel and cobalt, at much lower temperatures, typically 180-212°F (80-100°C), where steam pressure is minimal.

SUMMARY OF THE INVENTION

According to the invention there is provided a process for the extraction of nickel and cobalt from a laterite ore comprising the steps of reacting the ore, in slurry form, with sulphur dioxide to convert the iron, nickel and cobalt in the ore to soluble sulphates and bisulphites contained in a product slurry.

The laterite ore may first be treated to extract a limonite portion therefrom, which limonite portion is reacted with said sulphur dioxide.

The step of reacting the ore with sulphur dioxide may comprise a first stage SO_2 absorption in which a slurry of the ore and water is contacted with a mixture of SO_2 and N_2 such as from combustion of sulphur or sulphide minerals in air, followed by a second stage SO_2 absorption in which the slurry from the first stage is contacted with substantially 100% SO_2 gas and a pressure leach stage in which the slurry from the second stage SO_2 absorption is subjected to an elevated temperature and pressure.

Further objects and advantages of the invention will become apparent from the description of a preferred embodiment of the invention below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of one embodiment of the process according to the invention.

Figure 2 is a flow diagram of another embodiment of the process according to the invention.

Figures 3 to 5 are flow diagrams illustrating an embodiment of the process in more detail.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The process according to the invention will first be described generally with reference to Figures 1 and 2 and then in somewhat more detail with reference to Figures 3 to 5.

With reference to Figure 1, the process comprises a SO_2 absorption step 12 in which a slurry of limonite nickel-cobalt ore and water is contacted with SO_2

at or below ambient temperature. The next step is a pressure leaching step 14 at a temperature of from 180° - 212°F (80 - 100°C) and a SO_2 partial pressure of 80-200 psig (550 - 1400 kPa (gauge)) to substantially completely dissolve the metallic oxide components of the limonite, such as iron, nickel, cobalt, magnesium and manganese, as the soluble sulphates and bisulphites, according to the following reaction:

$$2MO.OH + 3SO_2\ (aq) \rightarrow MSO_4\ (aq) + M(HSO_3)_2\ (aq), \qquad (1)$$

where M = Fe, Co, Ni.

Magnesium, aluminum and other metallic oxides of limonite are similarly dissolved. These components are not oxidized or reduced so that they are also present as sulphates or bisulphites.

After the pressurized leach 14, the leach slurry is released to near atmospheric pressure and heated in an atmospheric SO_2 stripping step 16, to decompose the metal bisulphites according to the following reaction:

$$M(HSO_3)_2\ (aq) \rightarrow MSO_3(s) + SO_2(g), \qquad (2)$$

where M represents a metal, such as Fe, Ni, Co, Mg and Mn. Advantageously, part of the insoluble metal sulphates formed in step 16 is recycled to the SO_2 absorption step 12 to facilitate the absorption by the following buffering reaction (but this step is optional):

$$FeSO_3(s) + SO_2(g) + H_2O \rightarrow Fe(HSO_3)_2\ (aq). \qquad (3)$$

After the SO_2 stripping step 16, the slurry is subjected to a reaction step 18 with an acid ferric sulphate recycle stream to maximize recovery of sulphur dioxide by leaching of insoluble sulphites:

$$MSO_3(s) + H_2SO_4\ (aq) \rightarrow MSO_4(aq) + SO_2(g), \qquad (4)$$

where M represents a metal.

The slurry is then subjected to oxidation and hydrolysis (oxydrolysis) 20 to precipitate iron as jarosite with concurrent generation of free sulphuric acid and iron (III) sulphate:

$$3FeSO_4\ (aq) + 3/4\ O_2 \rightarrow HFe_3(SO_4)_2(OH)_6(s) + H_2SO_4, \qquad (5)$$

$$H_2SO_4 + 2FeSO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O. \qquad (6)$$

The product of the oxyhydrolysis step 20 is passed to a thickener 22 and part of the acidic solution is recycled to effect the reaction step 18. If desired, the jarosite can be separated in an optional liquid/solid separation step at this stage for disposal or use.

The balance of the oxydrolysis product is treated in a neutralization step 24 with acid neutralizing material, advantageously saprolite or garnierite containing nickel and cobalt, to precipitate remaining iron as jarosite:

$$MgO + 3/4\ O_2 + 3FeSO_4\ (aq) \rightarrow HFe_3(SO_4)_2(OH)_6\downarrow + MgSO_4(aq), \qquad (7)$$

in which MgO represents active magnesia from the saprolite or garnierite. Other acid neutralizing materials, such as limestone or dolomite can also be used.

If the neutralization 24 is carried out in seawater or water containing significant amounts of a monovalent cation(s), jarosite precipitation is facilitated by, for example:

$$NaCl\ (aq) + 3FeSO_4\ (aq) + 3/4\ O_2 \rightarrow NaFe_3(SO_4)_2(OH)_6 + H_2SO_4\ (aq) + HCl\ (aq). \qquad (8)$$

The neutralization step 24 is followed by a liquid/solid separation 26, to separate the jarosite and to produce a pregnant solution containing nickel and cobalt ions in solution, as indicated at 28.

Nickel and cobalt may be recovered from the solution 28 by one or a combination of known methods, such as sulphide precipitation, liquid ion exchange, i.e. solvent extraction and stripping or hydrous oxide and/or carbonate precipitation, which may optimally be followed by ammonia leaching and separate recovery of nickel-cobalt salts or metals.

In a particular embodiment of the invention, the SO_2 absorption step 12 is carried out in two stages 30 and 32, as shown in Figure 2. In this embodiment, the first stage 30 is carried out with an SO_2 - N_2 mixture typically generated by the burning of sulphur or roasting of sulphide minerals in air or oxygen enriched air. The second stage 32 is carried out with 100% SO_2 recycled from the steam stripping step 16 and the reaction step 18.

The gas from the first SO_2 absorption stage 30 is subjected to a SO_2 scrubbing step 33 to provide a gas which can be vented to atmosphere. During the scrubbing process the SO_2 is converted to H_2SO_4 which is used in the reaction step 18.

The process will now be described in more detail, by way of example, with reference to Figures 3 to 5. Referring to Figure 3, laterite ore is transferred from a stockpile 34 or directly from a mine truck 36 to a dump pocket 38 where it is slurried, as shown at 40, with salt water or sea water, or fresh water to which a source of monovalent jarosite stabilizing cations is added. However, if fresh water is used, the source of jarosite stabilizer is advantageously added after the thickener 56, which will be referred to below.

The slurry is passed to a rotary scrubber 41. By means of a trommel screen 42 on the scrubber 41 and sieve bends and cyclone, the ore is separated into primary fines 44, typically 0.5 mm, which is the limonite fraction of the ore, and oversize 46, which is mainly saprolite, i.e., partially weathered, high magnesium material, which is conveyed to a stockpile 47. The primary fines 44 are passed by a secondary screen 48, where further oversize is separated and conveyed to the stockpile 47.

The secondary fines from the screen 48 go to a pump box 50 from where they are pumped by pump 52 to a cyclone 54 for further separation in fines and oversize. The fines from the overflow of the cyclone 54 are passed to the thickener 56. The oversize from the cyclone underflow pass by a tertiary screen 62 where oversize is separated which is passed to the jarosite precipitation step 92 for utilization. The fines from the screen 62 go to pump box 64 from where they are pumped by pump 66 to the thickener 56.

The fine slurry of limonite which is passed to the thickener 56 is dilute and it is thickened or concentrated in the thickener 56 for pipeline transfer to

an SO_2 absorption stage, as indicated at 58. The thickener overflow, i.e. seawater diluted by the fresh water content of the raw ore, is discarded, as shown at 60.

In Figure 4, the limonite slurry from the thickener 56, again indicated at 58, is fed to a counter-current absorption tower 68 where it contacts SO_2 from an SO_2/N_2 mixture of about 20% SO_2 and about 80% N_2, which is also fed to the tower 68, as indicated at 70.

From the tower 68, the slurry, now in equilibrium with the SO_2 gas, passes to a second countercurrent absorption tower 72 to which is fed essentially 100% SO_2 gas from the SO_2 stripping of reduction autoclave product which is a later stage in the process and which will be described below. The slurry now equilibrates with the 100% SO_2 gas in the tower 72.

Gas exhausting from the first countercurrent tower 68 has residual SO_2 which must be scrubbed out before the gas can be exhausted. The SO_2 is reacted with excess air in an iron sulphate solution a shown as 74, to generate sulphuric acid, leaving an SO_2 free vent gas. The sulphuric acid produced is reacted with the $FeSO_3$ slurry from the SO_2 stripping step 80, which will be described below, for the optimization of SO_2 recovery.

From the tower 72, the limonite slurry, now saturated with SO_2 at or slightly above atmospheric pressure, passes to a reduction leach autoclave 76, where heat, such as in the form of steam, is supplied to accelerate or facilitate process reaction (1) above.

The autoclave 76 operates at 180-212°F (80-100C°) and up to 250 psig (1725 kPa (gauge)) pressure.

The reduced slurry exiting the autoclave 76 is indicated at 78.

Figure 5 shows the reduced slurry 78 passing to a series of SO_2 strip tanks 80 operated at slightly above atmospheric pressure in which steam drives off dissolved and reactive SO_2, e.g.,

$$Fe(HSO_3)_2\ (aq) \rightarrow FeSO_3(s) + SO_2(g) \qquad (9)$$

The essentially 100% SO_2 gas from the strip tanks 80 is cooled in a cooler (not shown) and recycled to the second absorption tower 72, as indicated at 82.

The stripped slurry passes to an oxydrolysis autoclave 84 in which reaction with oxygen produces jarosite essentially free of Ni and Co. The jarosite is filtered by a drum filter 86 and pumped, by pump 88 to a tailing pond as shown at 90.

The acidic solution from the filtration is further treated with prepared finely crushed saprolite to eliminate iron in a secondary jarosite precipitation stage, according to reaction aquation (7) above, and as indicated at 92.

The product of the secondary precipitation stage 92 is passed to a mixing tank 94 and pumped by pump 96 to a drum filter 98 to separate the solids from the secondary separation 92, which solids are disposed of, as indicated at 100.

The liquid product from the filter 98 is the pregnant solution which is the product of the process containing the nickel and cobalt ions in solution and indicated at 102.

While only preferred embodiments of the invention have been described herein in detail, the invention is not limited thereby and modifications can be made within the scope of the attached claims.

WHAT IS CLAIMED IS:

1. A process for the extraction of nickel and cobalt from a laterite ore comprising the step of reacting the ore, in slurry form, with sulphur dioxide to convert the iron, nickel and cobalt in the ore to soluble sulphates and bisulphites contained in a product slurry.

2. The process according to claim 1, wherein the laterite ore is first treated to extract a limonite portion therefrom, which limonite portion is reacted with said sulphur dioxide.

3. The process according to claim 2, wherein said treatment comprises producing a limonite slurry, which comprises said limonite portion and water, which limonite slurry is reacted with said sulphur dioxide to produce said product slurry containing said sulphates and bisulphites.

4. The process according to claim 3, wherein said water comprises sea water.

5. The process according to claim 3, further comprising the step of adding a source of monovalent jarosite stabilizing cations to said product slurry.

6. The process according to claim 1, further comprising the step of heating said product slurry to decompose said bisulphites to produce insoluble metal sulphites and SO_2 gas.

7. The process according to claim 6, further comprising the step of recycling said SO_2 gas for reaction with the ore.

8. The process according to claim 6, further comprising the step of reacting said soluble sulphates with oxygen or air to oxidize dissolved iron sulphate to jarosite with concurrent generation of a solution of sulphuric acid and iron III sulphate.

9. The process according to claim 8, further comprising the step of reacting said insoluble metal sulphites with sulphuric acid to produce soluble sulphates and SO_2 gas.

10. The process according to claim 9, further comprising the step of recycling said SO_2 gas for a reaction with said ore.

11. The process according to claim 9 wherein the reaction of said insoluble metal sulphites with sulphuric acid is effected with a part of the solution of sulphuric acid and iron III sulphate from said iron sulphate oxidation to jarosite.

12. The process according to claim 8, further comprising the step of reacting said solution of sulphuric acid and iron III sulphate with a base to precipitate iron as jarosite and producing a solution of nickel and cobalt sulphates.

13. The process according to claim 12, wherein said base comprises a high magnesium fraction of laterite nickel deposit.

14. The process according to claim 13, wherein said base comprises saprolite.

15. The process according to claim 14, wherein said base comprises garnierite.

16. The process according to claim 13, wherein said base further comprises a reactive mineral carbonate.

17. The process according to claim 16, wherein said reactive mineral carbonate is selected from the group consisting of calcite, dolomite, magnesite and ankerite.

18. The process according to claim 1, wherein said step of reacting the ore, in slurry form, with sulphur dioxide comprises a first stage SO_2 absorption in which a slurry of the ore and water is contacted with a mixture of SO_2 and N_2, a second stage SO_2 absorption in which the slurry from the first stage is contacted with substantially 100% SO_2 gas and a pressure leach stage in which the slurry from the second stage SO_2 absorption is subjected to an elevated temperature and pressure.

19. The process according to claim 18, in which the elevated temperature is from about 180° to about 212°F and the pressure is a SO_2 partial pressure of from about 80 to about 200 psig.

20. The process according to claim 18, further comprising the step of heating said product slurry to decompose said bisulphites to produce insoluble metal sulphites and SO_2 gas.

21. The process according to claim 20, further comprising the step of recycling said SO_2 gas to said second stage SO_2 absorption.

22. The process according to claim 20, further comprising the step of recycling part of said insoluble metal sulphites to said first stage SO_2 absorption.

23. The process according to claim 20, further comprising the step of reacting said soluble sulphates with oxygen or air to oxidize dissolved iron sulphate, thereby to precipitate jarosite with concurrent generation of a solution of sulphuric acid and iron III sulphate.

24. The process according to claim 23, further comprising the step of reacting said insoluble metal sulphites with sulphuric acid to produce soluble sulphates and SO_2 gas.

25. The process according to claim 24, further comprising the step of recycling said SO_2 gas to said second stage SO_2 absorption.

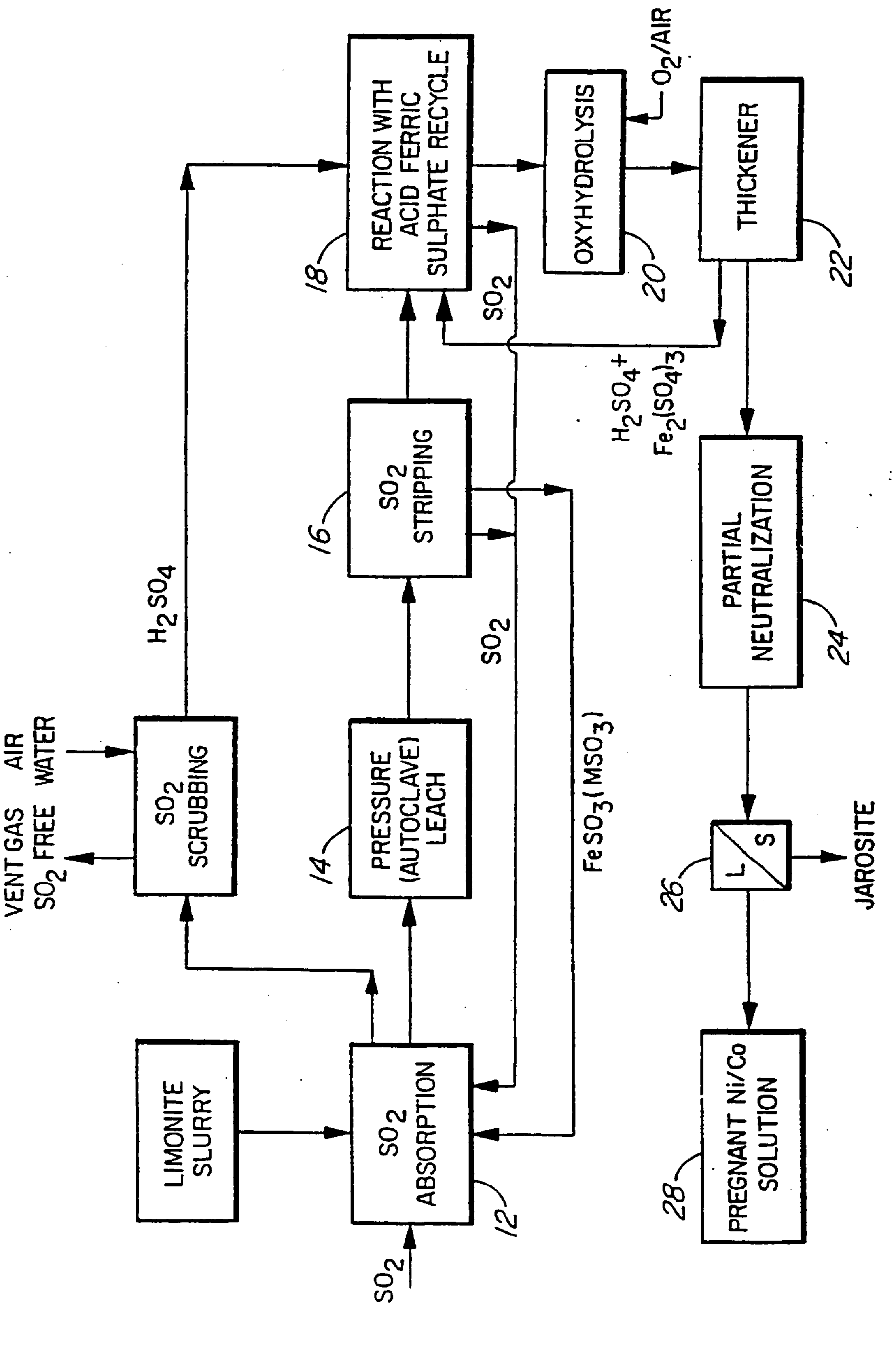
LIMONITE SLURRY
SO2 ABSORPTION
12
SO2
PRESSURE (AUTOCLAVE) LEACH
14
SO2 STRIPPING
16
REACTION WITH ACID FERRIC SULPHATE RECYCLE
18
OXYHYDROLYSIS
20
O2/AIR
THICKENER
22
H2SO4 + Fe2(SO4)3
PARTIAL NEUTRALIZATION
24
L S
26
JAROSITE
PREGNANT Ni/Co SOLUTION
28
SO2 SCRUBBING
VENT GAS SO2 FREE
AIR WATER
H2SO4
SO2
SO2
FeSO3 (MSO3)

FIG. 1

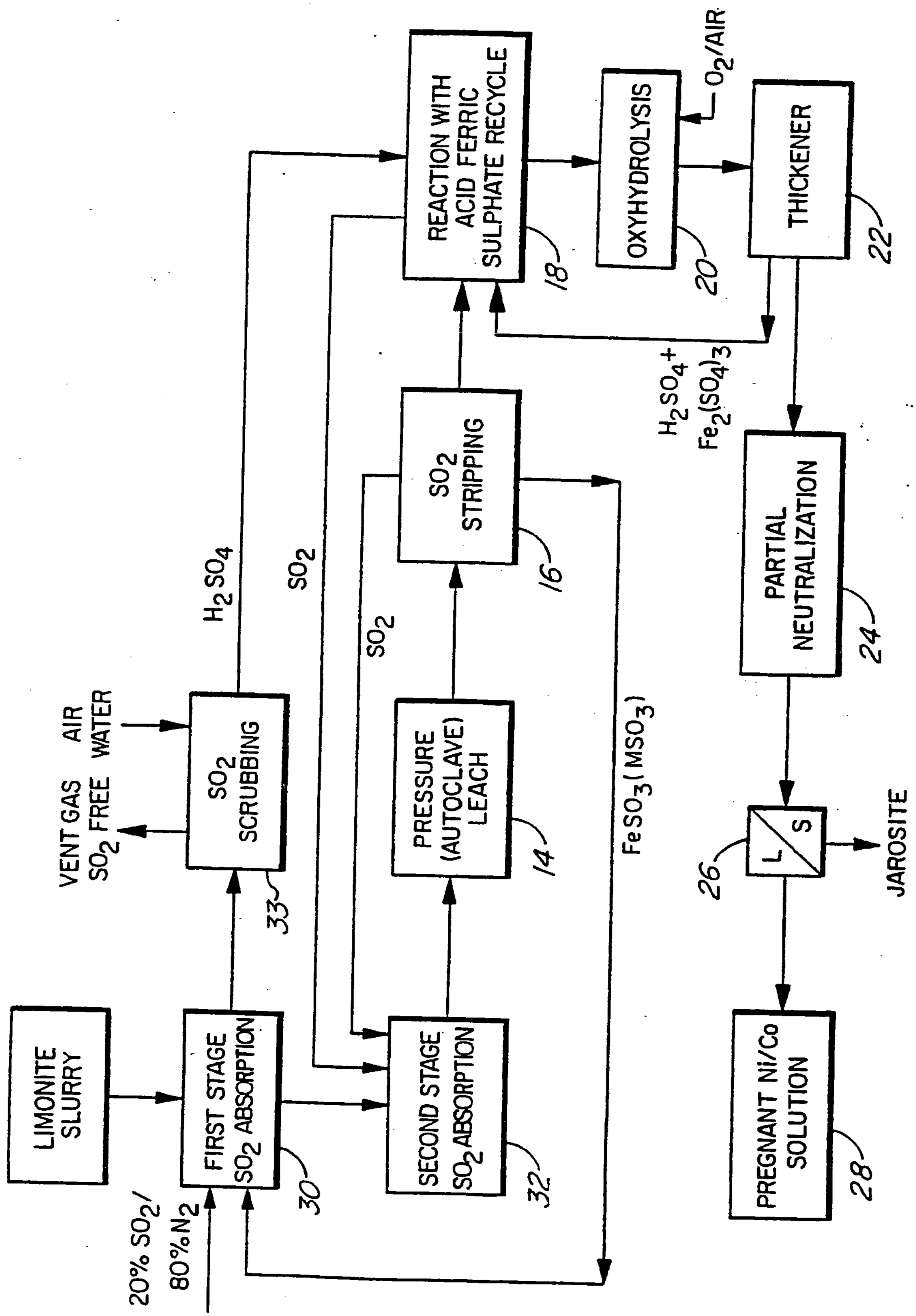
LIMONITE SLURRY
FIRST STAGE SO_2 ABSORPTION
30
20% SO_2/ 80% N_2
SO_2 SCRUBBING
33
VENT GAS SO_2 FREE
AIR WATER
H_2SO_4
SO_2
SECOND STAGE SO_2 ABSORPTION
32
SO_2
PRESSURE (AUTOCLAVE) LEACH
14
SO_2 STRIPPING
16
$FeSO_3$ (MSO_3)
REACTION WITH ACID FERRIC SULPHATE RECYCLE
18
OXYHYDROLYSIS
20
O_2/AIR
THICKENER
22
H_2SO_4 + $Fe_2(SO_4)_3$
PARTIAL NEUTRALIZATION
24
L S
26
JAROSITE
PREGNANT Ni/Co SOLUTION
28

FIG. 2

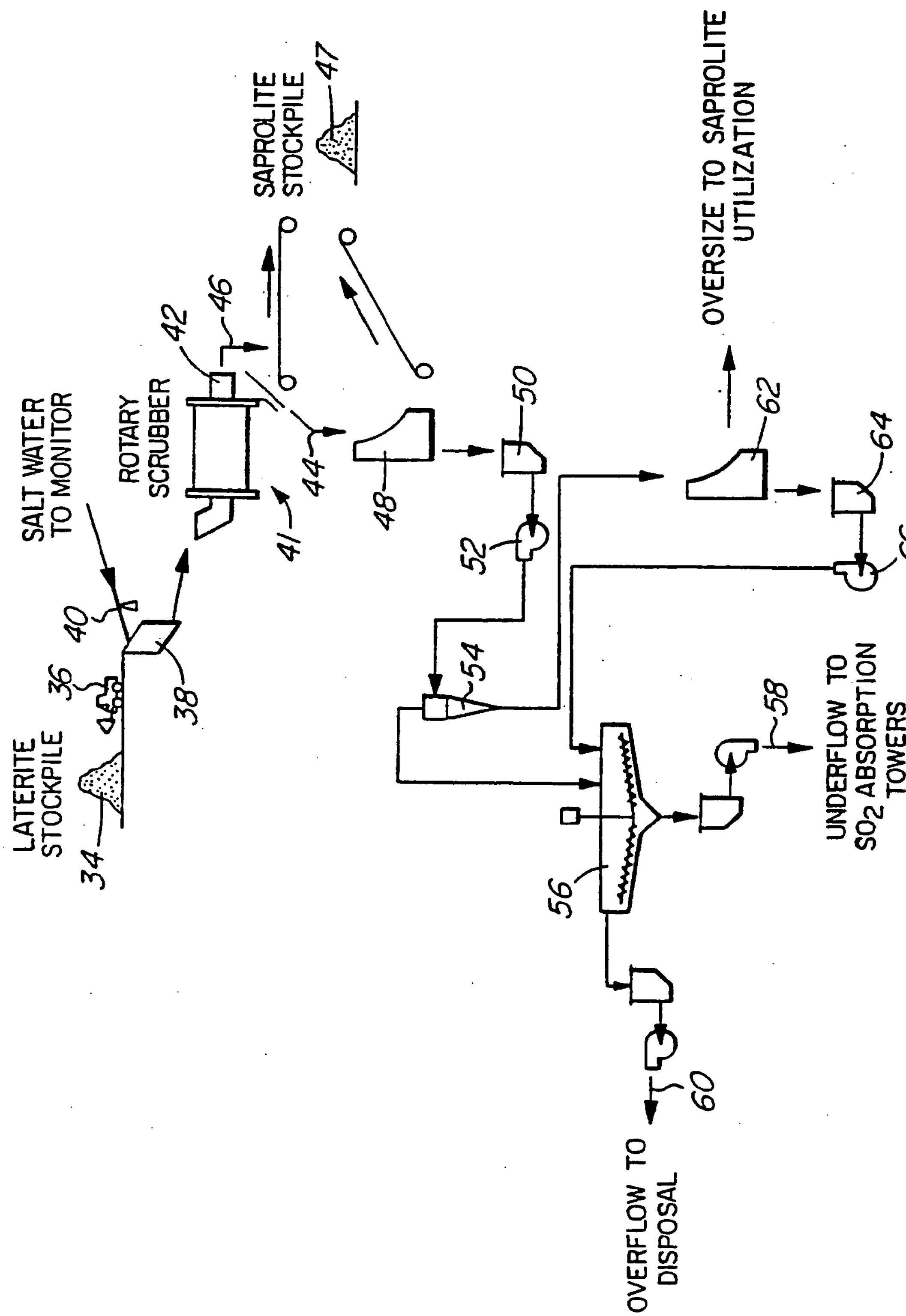
LATERITE STOCKPILE
34
36
38
40
SALT WATER TO MONITOR
ROTARY SCRUBBER
41
42
44
46
SAPROLITE STOCKPILE
47
48
50
52
54
56
58
60
62
64
66
OVERSIZE TO SAPROLITE UTILIZATION
UNDERFLOW TO SO_2 ABSORPTION TOWERS
OVERFLOW TO DISPOSAL

FIG. 3

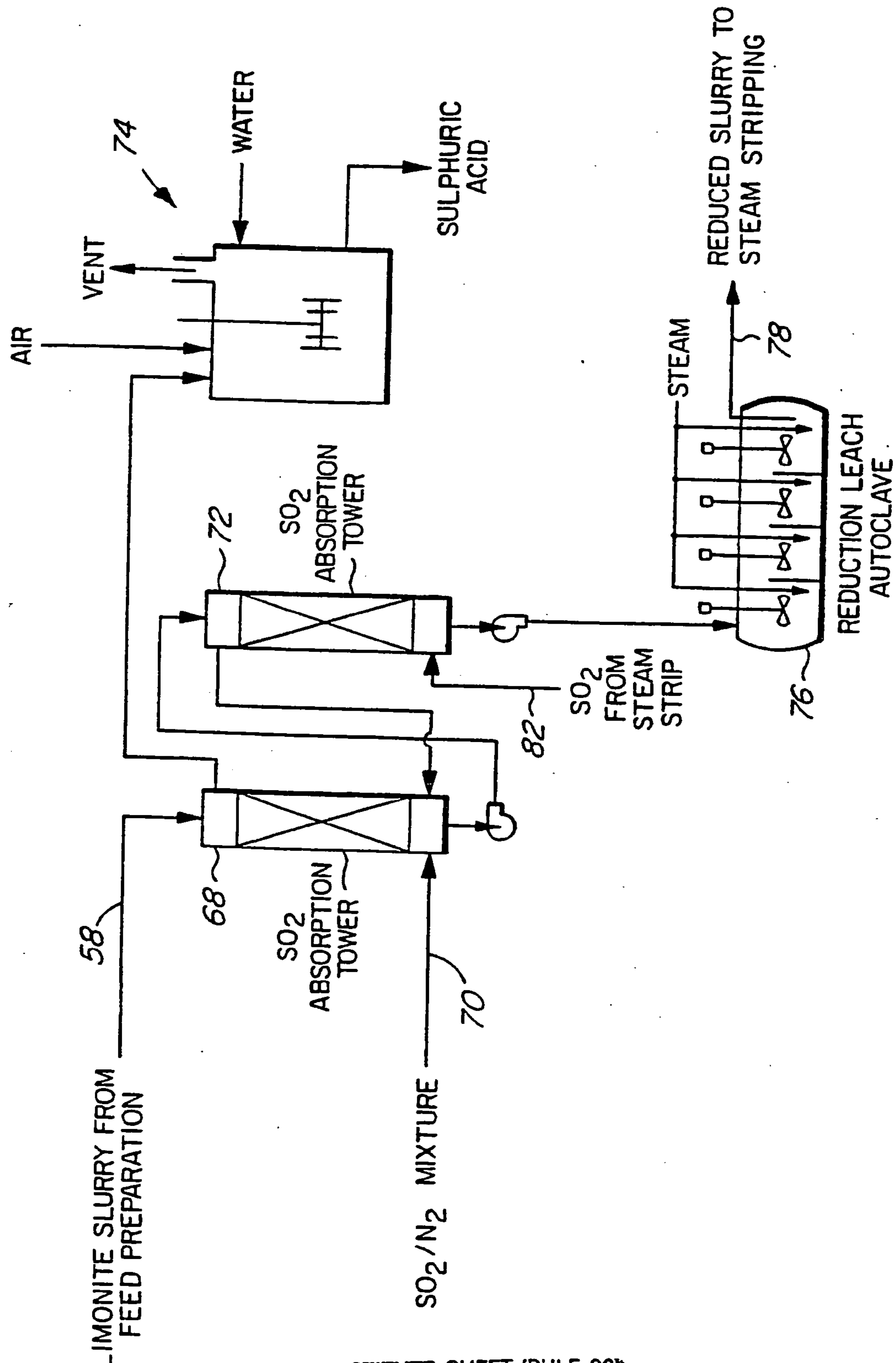
LIMONITE SLURRY FROM FEED PREPARATION
58
68
SO_2 ABSORPTION TOWER
SO_2/N_2 MIXTURE
70
72
SO_2 ABSORPTION TOWER
82
SO_2 FROM STEAM STRIP
AIR
VENT
74
WATER
SULPHURIC ACID
STEAM
REDUCED SLURRY TO STEAM STRIPPING
78
REDUCTION LEACH AUTOCLAVE
76

FIG. 4

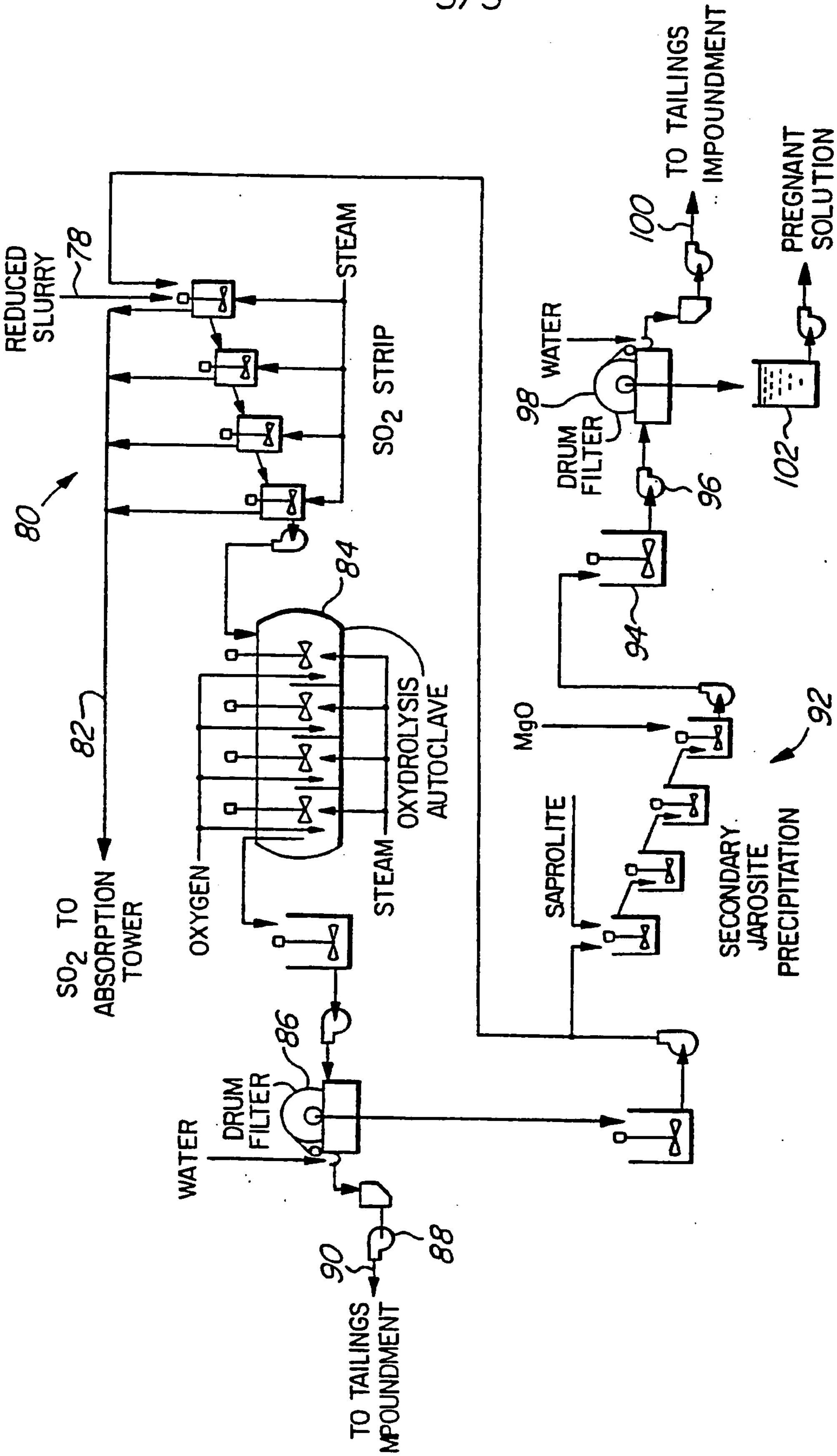
REDUCED SLURRY
78
STEAM
SO2 STRIP
80
84
OXYDROLYSIS AUTOCLAVE
82
SO2 TO ABSORPTION TOWER
OXYGEN
STEAM
86
DRUM FILTER
WATER
88
90
TO TAILINGS IMPOUNDMENT
TO TAILINGS IMPOUNDMENT
100
PREGNANT SOLUTION
WATER
98
DRUM FILTER
102
96
94
MgO
92
SAPROLITE
SECONDARY JAROSITE PRECIPITATION

FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00364

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22B3/08 C22B23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 169 856 (MERO) 16 February 1965 see claims ---	1
X	GB,A,898 993 (THE INTERNATIONAL NICKEL COMPANY OF CANADA LIMITED) 20 June 1962 see claims ---	1
X	US,A,3 869 360 (KANE WILLIAM S ET AL) 4 March 1975 see claims ---	1
X	US,A,4 280 986 (ZEITLIN HARRY ET AL) 28 July 1981 see claims ---	1
X	US,A,3 906 075 (MENZ DIETER) 16 September 1975 see claims ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 September 1996	27.09.96

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/CA 96/00364

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 064 248 (SHERRIT GORDON MINES LIMITED) 5 April 1967 see claims ---	1
X	DATABASE WPI Section Ch, Week 7736 Derwent Publications Ltd., London, GB; Class M25, AN 77-63484Y XP002013169 & JP,A,52 070 902 (DEEPSEA VENTURES INC) , 13 June 1977 see abstract ---	1
A	GB,A,996 472 (YAWATA IRON & STEEL COMPANY LIMITED) 30 June 1965 see claims -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 96/00364

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GB-A-898993		NONE		
US-A-3869360	04-03-75	US-A-	3810827	14-05-74
US-A-4280986	28-07-81	NONE		
US-A-3906075	16-09-75	AU-B-	461926	12-06-75
		AU-A-	4735772	11-04-74
		CA-A-	968567	03-06-75
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		FR-A-	2156079	25-05-73
		GB-A-	1412640	05-11-75
		JP-A-	48061311	28-08-73
GB-A-1064248		NONE		
GB-A-996472		NONE		